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Final Technical Report : November 1st 1961 - 31st October 1962.

Studies in Ion Solvation in Mixed Solvents

Contract number: DA-91-591-EUC-1973

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Abstract (i)

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Abstract

Using the appropriate chemical cells, the free energies of transfer of the pairs of ions H^+Br^- and H^+I^- in the standard state have been determined for transfers from water to 10% and 43.12% mixtures of methanol and water. By-products of the measurements are the activity coefficients of hydrobromic acid and the dissociation constants of boric acid in the two mixed solvents.

One important experimental difficulty has been overcome in these measurements. Some component of the methanol solutions is reduced if hydrogen electrodes of high catalytic activity are used. It has not yet been possible to show what this component is, but it is conceivable that methanol itself is reduced to methane under these conditions. This reduction affects the performance of the electrode, but reversible behaviour may be ensured in two ways. Firstly, lightly platinised electrodes may be used with fast rates of passage of hydrogen through the cell compartment. Secondly, electrodes of bare platinum, activated by polishing and oxidation with aqua regia, which have a low catalytic activity, may be used. Normally cell e.m.f's. are means of values obtained by both methods.

Using the present results, together with values obtained from the literature, it has been possible to compare free

energies of transfer from water to the mixed solvents for the pairs of ions, H^+Cl^- , H^+Br^- and H^+I^- with those for Li^+Cl^-, Na^+Cl^- and K^+Cl^-. Enthalpy data is also available in the literature and has enabled the comparison of the corresponding enthalpies and entropies of transfer with the free energy data.

The following pattern has emerged. For transfers from water to 10% methanol, the free energies of transfer for the three halide pairs lie on a straight line when plotted against r_-^{-1}, the reciprocal of the anion radius. This behaviour is qualitatively that expected from Born's equation, but the slope of the line is some ten times that predicted on this basis. An extrapolation to $r_-^{-1}=0$ yields an intercept which is tentatively identified with the free energy of transfer of the proton from water to 10% methanol. The sign of this suggests that,contrary to the simple electrostatic theory, the proton is in a lower free energy state in the mixed solvent than in water. If the free energies of transfer for the alkali chloride pairs are plotted against r_+^{-1}, the reciprocal of the cation radius, the slope of the line is of a sign opposite to that predicted by Born's equation. If, however, the cations, like the proton, are more stable in the mixed solvent than in water itself, and are stabilised to an extent proportional to r_+^{-1}, then the observed behaviour is reasonable.

The extrapolation of this line to $r_+^{-1}= 0$ therefore seems justified, and the intercept is identified with the free energy of transfer of the chloride ion. Using the value so obtained, a value for the free energy of transfer of the proton can be found which is in good agreement with the one obtained from the first extrapolation. A mean value is used as a basis for separating the free energies of transfer for pairs of ions into individual ionic values.

A similar procedure is adopted for the transfers from water to 43.12% methanol, and although in this case the graph of the free energy of transfer of the hydrogen halide ion pairs against r^{-1} is not so good a straight line, the agreement of single ion values from the two extrapolations is satisfactory.

The single ion values indicate that transfers of halide ions from water to the mixed solvents are very strongly disfavoured, the free energies of transfer being some ten times those predicted by Born's equation. In contrast, the transfer of positive ions favoured, though normally to a smaller extent.

This striking result is in close qualitative agreement with the work and conclusions of Grunwald, Baughman and Kohnstam, working with dioxan—water systems, who used different experimental techniques and a completely different method of obtaining individual ionic values.

These results are discussed and explained on the assumption that the solvation of the ions is dominated by an acid-base interaction between the ion and the solvent molecules, rather than by ion-dipole interactions or ion-dielectric interaction, though the latter will play some part.

Because of the inductive release of the methyl group, the methanol molecule will be a stronger base than the water molecule and will therefore solvate cations more efficiently than water. The reverse will be true for anions, as the methanol molecule is a weaker acid than the water molecule. These assumptions about the basicity and acidity of methanol are not generally accepted, but no method exists whereby these quantities can be determined directly or even estimated with confidence.

No clear pattern emerges for the enthalpies and entropies of transfer, and a reason for this is advanced.

An account of some preliminary work on dioxan-water mixtures is given in a special section.

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1. Introduction

1.1 Objectives and progress.

The objectives of the work were to study the behaviour of the pairs of ions

$$\left.\begin{array}{l} H^+,\ Cl^- \\ H^+,\ Br^- \\ H^+,\ I^- \end{array}\right\} \text{Group A} \qquad \left.\begin{array}{l} H^+,\ OH^- \\ Li^+,Cl^- \\ Na^+,Cl^- \\ K^+\ ,Cl^- \end{array}\right\} \text{Group B}$$

in methanol-water and dioxan-water mixtures by two techniques. (1) E.m.f. measurements on the appropriate chemical cells to deduce the free energy changes and changes in related thermodynamic quantities associated with the transfer of the various pairs of ions from water to the mixed solvent systems. (2) Measurements, either direct or indirect, of the so-called Washburn numbers of the electrolytes in these systems. The Washburn number is not a familiar property, and may be briefly explained as follows.

When a current is passed through an aqueous solution of a strong electrolyte (e.g. sodium chloride) to which a non-electrolyte (e.g.methanol) has been added, a net transport of methanol relative to water, or vice versa, will be observed in a particular direction, anodic or cathodic. This arises because of the different extents to which the ions interact with the water and methanol molecules.

The number of moles of non-electrolyte transported per Faraday of electricity passed is termed the Washburn number of that species.

It has not yet proved possible to make any measurements of Washburn numbers, owing to lack of time and personnel, although it is hoped to do so in the near future. Considerable progress has been made with the first objective, and the experimental work reported is entirely e.m.f. work in the two types of solvent mixture on electrolytes of group A. No work has yet been started on those in group B.

1.2 E.m.f. work.

If the standard e.m.f. of the cell

$$H_2 \,|\, HX \,|\, AgX\text{-}Ag$$

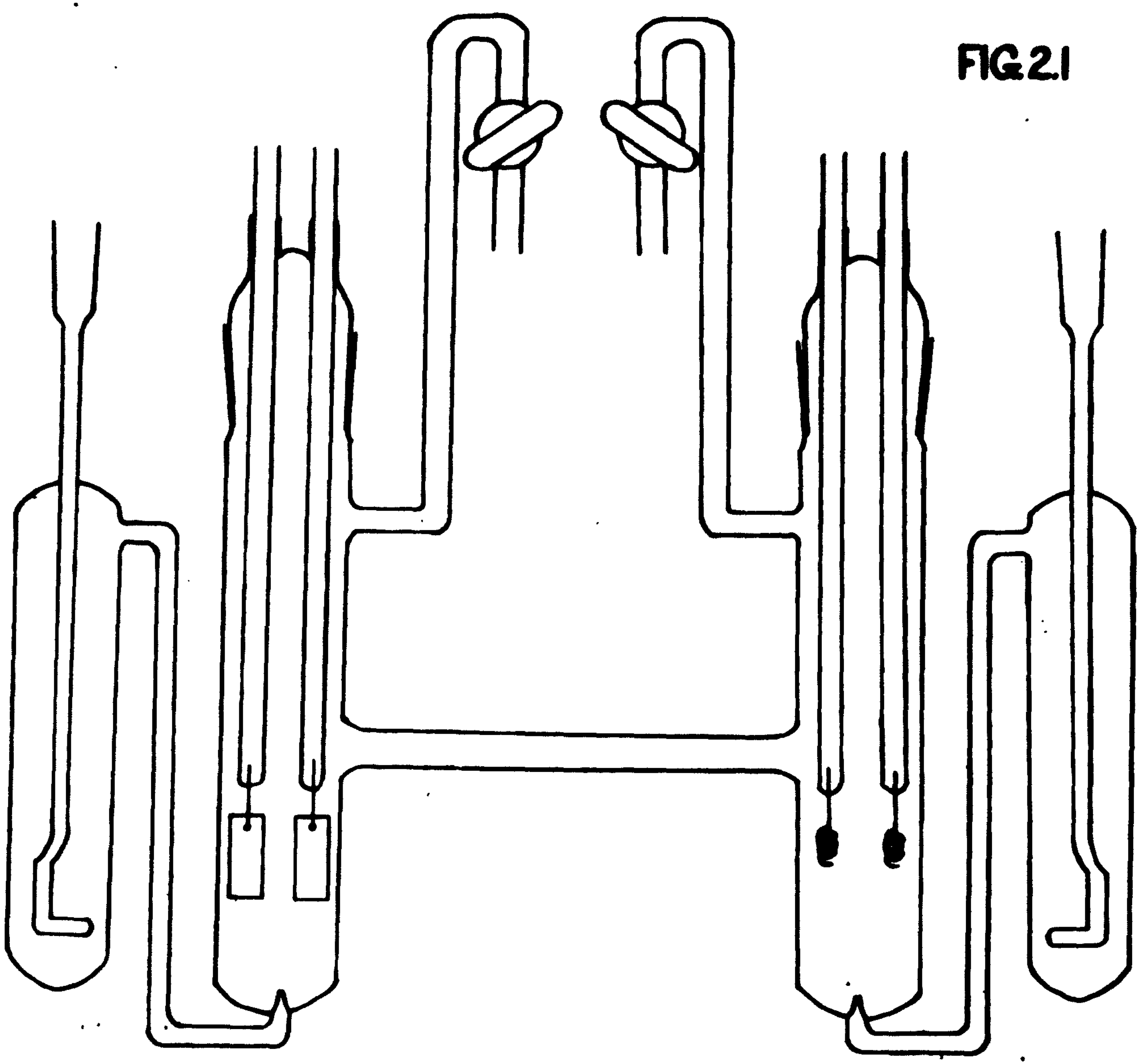
is measured in pure water $({}^{w}E^{o})$ and in some other solvent (e.g. a methanol-water or dioxan-water mixture) $({}^{s}E^{o})$ then the difference in solvation energy of the pair of ions H^+, X^- in the two media, or free energy of transfer in the standard state

$$\Delta G_t = F\,({}^{w}E^{o} - {}^{s}E^{o}).$$

From measurement of e.m.f. at various temperatures, ΔS_t and ΔH_t may also be computed.

The problem therefore devolves upon obtaining the standard e.m.fs of the above cell in the various solvent media, those in aqueous solution being well-established. In general, also, the standard e.m.fs. in the hydrochloric acid systems are also in the literature, so that the new measurements are largely on the bromide and iodide systems.

FIG.2.1



2. Experimental.

2.1 Accuracy of measurements.

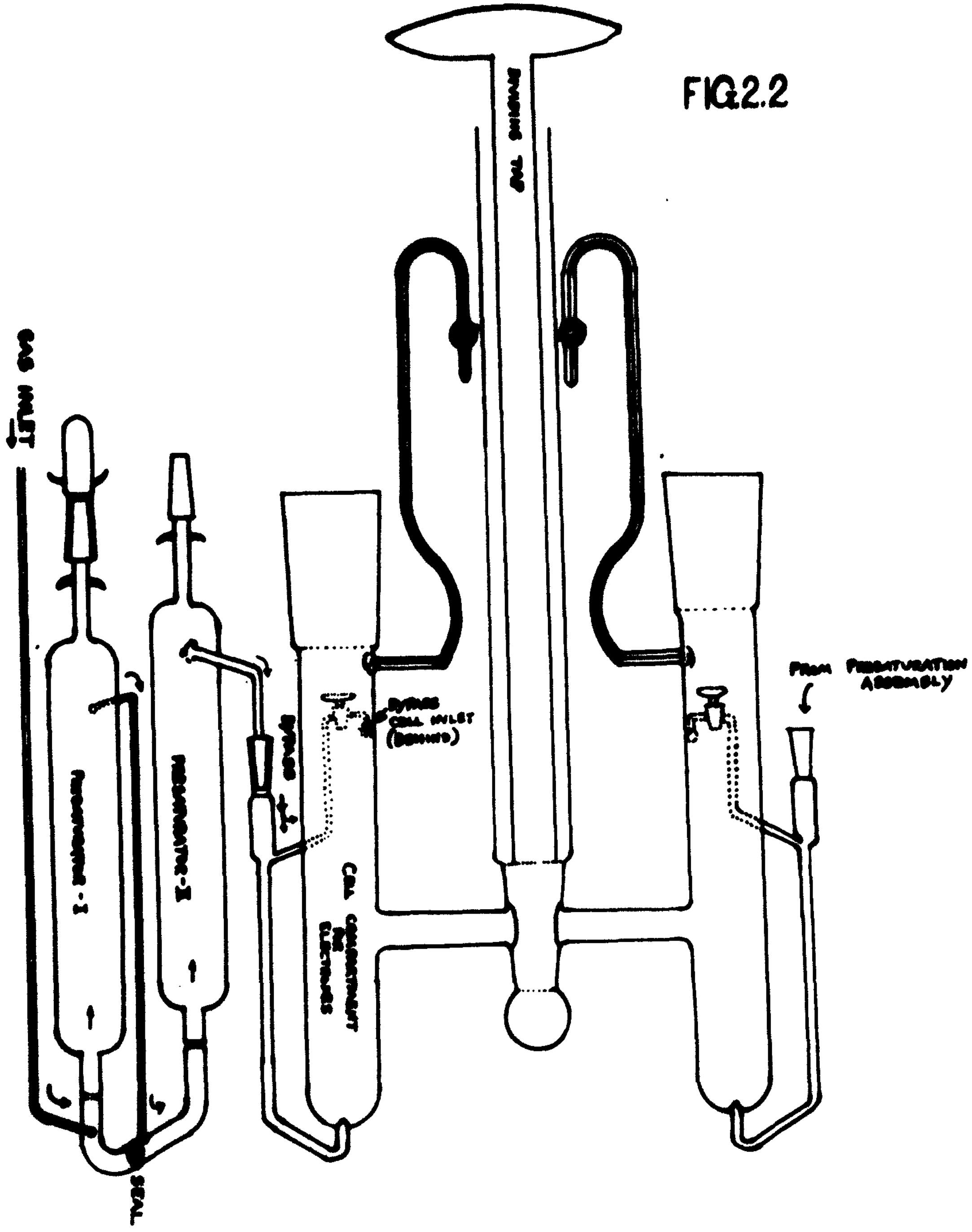
In methanol-water mixtures, two concentrations of methanol have been employed, 10% and 43.13% by weight. For the time being measurements have been made only at one temperature, 25°, and the e.m.f. data is of sufficient accuracy for theoretical discussion, if it is precise to ± 0.1mv or better for the 10% solution, and to about ± 0.2 mv. for the 43.12% solution.

In the dioxan-water mixtures, an attempt is being made to measure e.m.f. over a range of temperatures from 5°-45°, and a much higher precision is required if accurate values of ΔS_t and ΔH_t are to be obtained from the results. Good cell stability in time is essential, as any series of measurements may take from 2-3 days.

2.2 Cell design.

A simple type of cell, suitable for the methanol-water work, is shown in figure 2.1. The cell proper consists of hydrogen and silver-silver halide electrode compartments connected by a cross-piece. The electrodes, two for each compartment, are mounted with PVC sleeves into adaptors made from standard cone joints, which fit into the sockets at the head of each cell compartment. Hydrogen gas, passed through a commercial de-oxygenating cartridge, is delivered to both cell compartments via pre-saturators fused directly to them, and escapes through capillaries fitted with taps. Nitrogen gas can be substituted

FIG.2.2


SWINGING TAP
GAS INLET
PRESATURATOR - I
PRESATURATOR - II
BYPASS
BYPASS CELL INLET (BEHIND)
CELL COMPARTMENT FOR ELECTRODES
FROM PRESATURATION ASSEMBLY
SEAL

for hydrogen in the silver-silver halide compartments, if desired. The whole apparatus is immersed in a water bath kept to within ± 0.01° of 25°. It is perfectly satisfactory for work of limited precision.

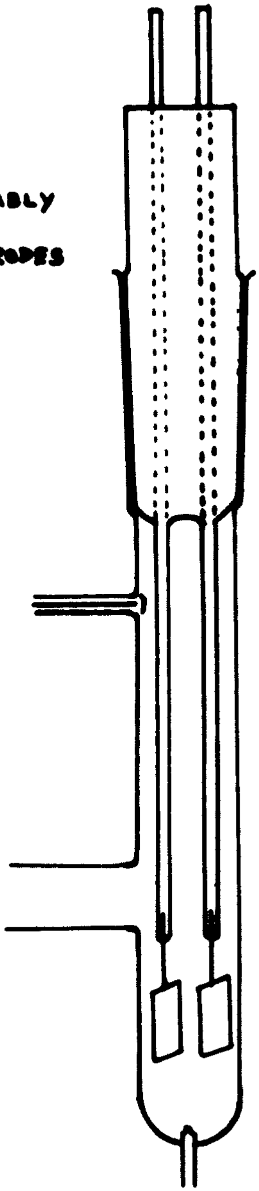
A cell suitable for the more precise dioxan-water work is shown in figure 2.2. Each one of the modifications of the simpler cell described has been dictated by necessity. The gas-saturation arrangements are modified by supplying two pre-saturators to each cell compartment, and by arranging for the gas to pass over the surface of the solutions in the cell compartments whenever it is not actually necessary to bubble it through them. Preliminary measurements with a cell of the first type showed a slow drift over a period of days which could be attributed to a gradual concentration of the cell solution through inadequate gas pre-saturation. The new arrangements are thought to eliminate the risk of detectable concentration change occurring.

A tap in the middle of the cell is opened only when measurements are being taken. This prevents mixing of the contents of the two compartments, which could result in loss of dissolved hydrogen from the hydrogen electrode compartment, when nitrogen is used on the silver-silver halide electrode side, and diffusion of dissolved silver halide to the hydrogen electrode which would be poisoned thereby.

Greater care is taken with the purification of hydrogen

FIG. 2.3

ELECTRODE ASSEMBLY SHOWING HYDROGEN ELECTRODES



gas in these measurements. After leaving the commercial de-oxygenation cartridge, it passes first through potassium hydroxide, to remove carbon dioxide, and then over heated copper to remove the last traces of oxygen.

The electrodes, two for each compartment, are mounted on standard cones, see fig. 2.3. The electrode holders are all of Pyrex glass, except that the platinum wires are sealed through soft-glass and are connected through graded seals to the Pyrex portion of the holder. The cone joints fit into the corresponding sockets in the electrode compartments. The central tap, by-pass taps and the saturator filling cones and caps are all lightly greased with "Apiezon" grease, before placing the apparatus in a water-bath thermostatted to ± 0.01° at various temperatures.

2.3 Cell-filling.

In the case of the simple cell, the cell solution is simply poured into the various compartments, the electrode compartments are stoppered and hydrogen or nitrogen passed for about ½hr. before introducing the electrodes and beginning measurements.

For more precise measurements with the modified cell, the solution is first saturated with hydrogen and then passed into the various compartments of the cell. The flow of gases is begun and the electrodes are then introduced.

2.4 Electrodes

2.41 Hydrogen Electrodes.

These are prepared in two different ways.

(a) A plating solution containing 2% of "chloroplatinic acid" and 2N with respect to hydrochloric acid, but containing no lead salts is prepared. Platinum foils supported in glass tubing are made cathodes in this solution, at varying current densities and for varying times. A current density of 10 - 20ma./cm^2 in an electrolysis lasting 10 - 20 minutes produces a golden coloured or light grey deposit.[1] Such electrodes have been used in the dioxan-water mixtures.

(b) A much higher current density (about 0.1 amp/cm^2) for a shorter time, 2 minutes, produces a somewhat more granular deposit which is probably less catalytically active than the first type,[2] giving an electrode which is more suitable for the methanol-water systems (see later discussion).

In both cases, the electrodes are warmed in nitric acid after plating and then washed with distilled water and the cell solution before introducing them into the cell.

(c) Feakins and French[3] described an electrode suitable for measurements in solutions of reducible organic compounds. Platinum foils are first highly polished by laying them on a glass plate and rubbing them with the rounded end of a glass rod. The foils are then cautiously warmed in a 50%

aqua regia solution until this high polish is just destroyed. They are then transferred to warm concentrated nitric acid for about 30 seconds before being washed with distilled water, then with cell solution and introduced into the cell immediately.

2.42 Silver-silver halide electrodes.

It is common to find that individual silver-silver halide electrodes from batches prepared simultaneously under the same conditions, differ from each other in potential when placed in a solution containing the appropriate halide ions. The difference between a pair of electrodes is the bias potential of that pair. Perhaps the most important criterion of a satisfactory method of preparation of these electrodes is that these bias potentials shall be small. The properties of silver-silver halide electrodes have been extensively studied in this and in previous work in this department, and of the three main types of electrode, (i) totally electrolytic, (ii) totally thermal and (iii) thermal-electrolytic, type (iii) is by far the most satisfactory. Thermal-electrolytic electrodes have low bias potentials (rarely greater than 0.05mv and usually much less) come to equilibrium rapidly (with the exception of the iodide electrodes), their potentials are stable in time, they are reversible and above all, easy to prepare.

Platinum wires of diameter 0.02" and length 11cms, having their ends sealed into glass tubes, are formed into compact helices, 0.6 cm in diameter. Silver oxide is made by mixing dilute solutions of silver nitrate and potassium hydroxide, filtering, and washing the precipitate thoroughly with distilled water and then with conductance water. The oxide is then made into a paste with conductance water, and the helices filled and thinly coated with the paste. The electrodes are then placed in a muffle-furnace at 550-600° for about five minutes. This treatment converts the silver oxide to silver, and is repeated once or twice leaving a continuous coherent thin layer of silver on the outside of the spiral, and the spiral itself filled with a porous mass of silver.

The electrodes are then made anodes in a 0.1N solution of the appropriate hydrogen halide or potassium halide and a current of 2ma/electrode passed for 2-3 hours. The resulting electrodes are normally of a variety of colours other than white. They are washed with distilled water then with the cell solution and introduced into the cell.

2.5. Materials.

2.51 Dioxan

The preparation of this material will be described in the special section on dioxan.

2.52 Methanol.

Burroughs' A.R. methanol is refluxed for 3 hrs with 20 gm. of potassium hydroxide and 10 gm. of silver nitrate per litre. The methanol is distilled off onto anhydrous calcium sulphate and allowed to stand for a few days. It is then fractionally distilled in an atmosphere of nitrogen with rejection of substantial head and tail fractions, and stored in a desiccator.

2.53 Hydrobromic acid.

"AnalaR" hydrobromic acid is diluted to the composition of the constant boiling mixture and distilled in a nitrogen atmosphere. The middle third of the distillate is redistilled and is then free from bromine.

A stock solution of suitable strength (N 0.5M) is prepared by careful weight dilution of this acid, and then analysed gravimetrically. The stock solution is used in the preparation of the more dilute cell solutions, the constant - boiling acid in the preparation of the more concentrated ones.

2.54 Potassium chloride.

A cold saturated solution of the "AnalaR" salt is precipitated by passing in hydrogen chloride gas. The precipitate is filtered and the procedure repeated. The salt is then recrystallised twice from conductivity water, dried at 110° and kept in a desiccator over silica gel.

The purified salt, unlike the starting material, is free from bromide ions, as shown by the uranine test. The complete removal of bromide is essential when the salt is to be used with silver-silver chloride electrodes, as otherwise the potential of the electrode can be seriously affected.

2.55 Potassium iodide.

The "AnalaR" salt is twice re-crystallised from conductivity water at 60°. After drying it at 110° it is kept in a desiccator over silica gel.

2.56 Borax.

The "AnalaR" compound is used without further purification and is stored over a saturated solution of sodium bromide.

2.57 Conductance water.

Conductance water is prepared using a still of the type described by Stuart and Wormwell[4].

2.6 Potentiometry.

A Pye precision vernier potentiometer is used in conjunction with recently calibrated standard cells, and a sensitive galvanometer. Measurements can be made to ± 0.01 mv with this arrangement.

2.7 Principles of the measurement.

2.71 Hydrobromic acid.

The cell

$$H_2 | HBr(m) \quad S(X\%) \quad W(\overline{100-X\%}) | AgBr-Ag \qquad \text{(Cell I)}$$

is used at fixed solvent (S) to water (W) concentrations, with molalities (m) of HBr varying from 0.003-0.1m. The standard e.m.f. of the cell is found by extrapolation of the observed e.m.f. values.

2.72 Hydriodic acid.

Because of the ease with which hydriodic acid is oxidised, measurements must be made on cells buffered to a high pH. Borax, which on solution gives a half-neutralised solution of HBO_2 is used as buffer. This is Owen's[5] method. Measurements are made on the cells

$$H_2 | HBO_2(m)\ NaBO_2(m)\ KI(m) | AgI\text{-}Ag$$

and

$$H_2 | HBO_2(m)\ NaBO_2(m)\ KCl(m) | AgCl\text{-}Ag$$

It will be shown later that, if m is small,

$$E^0_{HI} = E^0_{HCl} + E^m_{HI} - E^m_{HCl}.$$

E^m_{HI}, E^m_{HCl} are the observed, and E^0_{HI} and E^0_{HCl} the standard e.m.f.s of the two cells.

2.8 Methanol-water systems.

2.81 Behaviour of Hydrogen electrodes.

The hydrogen electrodes have been troublesome in both cells, particularly in cell II. Some account of how the difficulties have been overcome may be of interest.

It is well known that conventional hydrogen electrodes [Sec.2.41, method (a)] are unsuited for measurements in solutions of organic materials which are reducible, for example, acetone.[2,3,6] The characteristic behaviour of these electrodes in such media has been described by a number of authors, and all agree on certain diagnostic features. The potential of the electrode is found to depend on the rate at which hydrogen is bubbled through the solution, being more negative the faster the rate. Electrodes rarely agree, partly because of adventitious differences in the catalytic activity of their surfaces, partly because if they are in different compartments, the rate of passage of hydrogen may be different or because the geometry of the half-cell seems to have some effect.

The measurements are also highly irreversible, and a balance-point on the potentiometer is difficult to find.

These effects are easily understood in terms of the removal of hydrogen from the surface and immediate vicinity of the electrode by the material being reduced, causing the potential of the electrode to move to more positive values. If the rate of supply of hydrogen to the electrode is increased then this depletion can be at least partly remedied, although in many cases a true reading, independent of the rate of passage of hydrogen, cannot be found.

In the past various methods have been used to overcome these difficulties, one being that of Feakins and French[2;3,6] who prepared electrodes of greatly reduced catalytic activity [Sec.2.41 method (c)], sufficient activity to give a reversible electrode being obtained from bare platinum by polishing and etching with aqua regia. These electrodes were used successfully in acetone-water mixtures, in which no other type of electrode was satisfactory.

Extensive measurements had been carried out in the present series before it was realised that the hydrogen electrodes were giving spurious results and that these could be attributed to the reduction of some species in the cell solution. References in the 1st Quarterly Report to trouble with hydrogen electrodes in the buffered cells can in fact be attributed to this cause.

Both in the bromide and iodide systems, the hydrogen electrode potentials are found to be dependent on the rate of passage of hydrogen through the solution. While the effect is nothing like as pronounced as with ketone-water systems, it is sufficiently serious to require elimination, especially in the buffered systems, which are much more seriously affected than the bromide systems. In the latter the hydrogen ion concentration is of the order of 10^{-1} - 10^{-3}gm.ions/litre, while in the buffered systems it is normally about 10^{-9} gm. ions/litre. Insofar as the exchange currents at the electrode are dependent on the hydrogen ion concentration they will be a factor of 10^{6}-10^{8} greater in the bromide than in the buffered solutions, and the electrodes will be far less resistant to disturbance in the buffered systems.

The effect is not very serious in the 10% and 43.12% bromide solutions, though it is present. It has never been reported in hydrochloric acid solutions in methanol, on which extensive studies have been done. In recent work done by the principal investigator[7] the effect was specifically tested for and not found, although this is not recorded in the publication. Subsequently we have re-examined the properties of hydrogen electrodes in methanolic hydrochloric acid systems, but there is no evidence of any reduction effect in a 43.12% mixture, although it may be present in solutions containing higher proportions of methanol. It is very marked in a hydrobromic acid solution containing 90% of methanol. Reduction can occur in the presence of chloride ions, however, as measurements on the buffered cell are seriously affected.

It is not yet clear what species in the solution is being reduced. It is known that methanol is rather easily oxidised to formaldehyde, and appreciable amounts of this impurity could give rise to the observed effects. Tests for formaldehyde in the samples of methanol used show a very low formaldehyde content (< 0.00025 moles/litre), and it therefore seems that formaldehyde is not introduced at this stage. When the hydrogen electrode first enters the solution, it must itself be in a highly oxidised condition and may oxidise some of the methanol. This possibility is under experimental examination.

A further possibility is that methanol is undergoing reduction to methane. It is known that hydrogenated Raney nickel will convert pure methanol to methane. We have attempted to demonstrate reduction of a typical cell solution by hydrogen in the presence of platinum black, by shaking these together for periods of several days in a closed vessel, admitting the gaseous phase to an infrared cell and looking for methane in the infrared spectrum. These experiments have so far yielded negative results. It should be stressed that even a very slow reduction will cause erratic electrode behaviour. Thus Feakins and French[6] showed that acetone in an acidified 40% mixture with water was reduced by platinum black only at the rate of 1% per hour at room temperature, yet hydrogen electrode measurements are quite impossible with ordinary electrodes. The effect with the methanol systems is much smaller than this. It may be noted that Moore and Felsing[8] were unable to make successful hydrogen electrode measurements in hydrochloric acid solutions containing 10% of n-propanol. The behaviour described is exactly that of a reducible system. Claussen and French[9] were later able to do these measurements, possibly because they made a practice of drying their hydrogen electrodes in hydrogen before use. This would not only reduce their catalytic activity, but also, if the reducible species were not the alcohol but the corresponding aldehyde, formed when the electrode entered the system, this would be less likely to form if a reduced electrode were used. Although this is, to some extent, a side-issue, it is hoped to identify the cause of the reduction effect. It is not necessary, of course, to have this information to be able to eliminate the trouble.

With reducible solutions it is usually observed that the potential of a platinised platinum hydrogen electrode becomes more negative, i.e. approaches the true equilibrium value, as the rate of flow of hydrogen is increased. With a highly reducible solution it is not possible to reach a rate of flow above which there is no further change in the potential of the electrode. With the methanol systems, however, this is possible. With a fairly brisk rate of flow the electrode comes to equilibrium within about two hours and a further increase in the flow-rate has no effect on the potential. Electrodes of type (b) (Sec. 2.41) are normally used in these measurements.

The electrodes described in sec.2.41(c), which may be designated "activated", since they depend on the activation of bare platinum, have also been used. These electrodes normally come to equilibrium within one hour. The cell e.m.f. is then steady to within ± 0.02 mv. for at least two or three hours, and often longer, even up to 24 hours, but, as may be expected, the average life of these electrodes is not as long as that of the more conventional type. These electrodes appear to effect little or no reduction of the solution, and are brought to equilibrium by quite slow rates of flow of hydrogen

In carrying out a measurement, an equilibrium value of the cell e.m.f. is found using one type of electrode, and the other is then substituted for it, and the equilibrium value again found. The order in which the electrodes are used is immaterial. The agreement between the two readings is normally within 0.1 mv, and the mean value is taken as the equilibrium e.m.f. of the cell.

2.82 Behaviour of Silver-silver bromide electrodes.

No particular difficulty has been experienced with these electrodes, although it must be noted that they are extremely sensitive to light. This sensitivity is much greater than that of silver-silver chloride or silver-silver iodide electrodes, and we have observed that exposure of an electrode to bright sunlight can cause its potential to shift to a value as much as 2-3 mv. more positive than the value in the dark. This photosensitivity is not commented on by the workers who have measured the standard e.m.f. of cell I in aqueous solution. Care has been taken to carry out all measurements in subdued lighting, or with the silver-silver bromide compartment covered against light.

2.83. Silver-silver iodide electrodes.

It has been observed that these electrodes, if freshly prepared, take some 6 hours to come to a steady potential in the cell. The shift is in the positive direction and is large (about 0.5mv.).

References.

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2. Feakins, Thesis, London, 1956.
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3. Results.

3.1 Treatment of Results.

3.11 All e.m.f. values are corrected to 1 atmosphere pressure of hydrogen by adding a quantity ΔE to the e.m.f. such that

$$\Delta E = \frac{k}{2} \cdot \frac{760}{P-\pi}$$

$$k = \frac{RT}{F} \log_e 10.$$

P is the atmospheric pressure in mm. and

π is the vapour pressure of the cell solution in mm.

3.12 Bromide results.

For the cell $H_2 | HBr | AgBr\text{-}Ag$

in a given solvent or solvent mixture

$$E = E^o_m - 2k\log\gamma_\pm m \qquad (1)$$

where E^o_m is the molal standard potential,

$\gamma_\pm$ is the mean ion activity coefficient

and m is the molality of hydrobromic acid.

From Debye-Hückel theory :

$$\log\gamma_\pm = \frac{-A\sqrt{c}}{1 + \mathring{a}B\sqrt{c}} + B'm - \log(1 + 0.002M_{xy}m) \qquad (2)$$

A and B are functions of the dielectric constant and temperature and may be calculated from the theory. $\mathring{a}$, the so-called distance of closest approach of the ions in Ångstrom units and B'are essentially empirical quantities. It is convenient to choose a value of 4.4 for $\mathring{a}$, the value used in aqueous solutions, leaving B' to be determined. M_{xy} is the mean molecular weight, c, the molarity, $= m\rho$, where ρ is the density of the solvent.

Substituting (2) in (1)

$$E = E^{o}_{m} - 2k\log m + \frac{2kA\sqrt{c}}{1 + \mathring{a}B\sqrt{c}} - 2kB'm + 2k\log (1 + 0.002M_{xy}m)$$

Rearranging, put

$$E + 2k\log m - \frac{2kA\sqrt{c}}{1 + \mathring{a}B\sqrt{c}} - 2k\log(1 + 0.002M_{xy}m) = E^{o\,'} = E^{o}_{m} - 2kB'm$$

If $E^{o\,'}$ is therefore plotted against m, a straight line of slope $-2kB'$, and intercept E^{o}_{m} should be obtained. This is found for both the bromide systems, the straight lines being found by the method of least squares. (The graphs are not reproduced here, but the constants E^{o}_{m} and B', derived from them are given). The accuracy on the E^{o}_{m} values is ± 0.07mv for the 10% solutions and ± 0.09mv for the 43.12% solutions.

With B' known, activity coefficients at rounded molalities can be calculated, and are displayed in table 4.

3.13 Iodide results.

For the cell

$$H_2|HBO_2(m)\ NaBO_2(m)\ KI(m)|\ AgI\text{-}Ag$$

$$E_I = E^{o}_{HI} - k\log K - k\log \frac{\gamma_{I^-}\gamma_{HA}}{\gamma_A} - k\log m \qquad (1)$$

and for the cell

$$H_2|HBO_2(m)\ NaBO_2(m)\ KCl(m)|AgCl - Ag$$

$$E_{Cl} = E^{o}_{HCl} - k\log K - k\log \frac{\gamma_{Cl^-}\gamma'_{HA}}{\gamma'_A} - k\log m \qquad (2)$$

If parallel measurements are made on the two cells, containing the appropriate mixed solvent, at the same molalities, m, then

$$E_I - E_{Cl} = E^o_{HI} - E^o_{HCl} - k\left[\log \frac{\gamma_I - \gamma_{HA}\gamma_{A-}}{\gamma_A - \gamma'_{HA}\gamma_{Cl-}}\right]$$

At low concentrations ($\ll$ 0.01m) the bracketed term may be expected to be not very different from zero. While, in principle, it is possible to eliminate its effect by extrapolating to m = 0, the deviations from a constant value of $E_I - E_{Cl}$ are in practice random with varying m and not systematic, and we therefore conclude that

$$E_I - E_{Cl} = E^o_{HI} - E^o_{HCl}$$

within the experimental error over the range studied here, namely 0.003m - 0.01m. The e.m.f.s. of the two cells were measured over this range, and using the literature value for E^o_{HCl}, E^o_{HI} was computed.

3.14 Dissociation constants of boric acid.

From equation (2) (3.13) we have :

$$-\log K - \log\frac{\gamma_{Cl}\gamma'_{HA}}{\gamma'_{A-}} = \frac{E_{Cl} - E^o_{HCl}}{k} + \log m = pK'$$

The quantity pK' is plotted against the ionic strength of the solution and the curve extrapolated to zero ionic strength to give a preliminary value of pK. A more rigorous extrapolation will be carried out later.

3.2 Numerical results.

Literature values accepted.

For the cell

$$H_2|HCl|AgCl - Ag$$

E^o_m (aqueous solution) = 0.22240volt (± 0.04mv.).

This is the mean of three independent and closely concordant values.[1]

E^o_m (10% methanol) = 0.21535 volt.[2]

E^o_m (43.12% methanol) = 0.1958 volt.

This last value is obtained from the E^o_m value in pure water and Schwab and Ziegenbalg's[3] data for the cell

$$H_2|HCl|Hg_2Cl_2 - Hg.$$

Their value is in good agreement with that of Feakins[5], but not with that of Austin, Hunt, Johnson and Parton[4] or Oiwa[6]. Schwab and Ziegenbalg's values are preferred because no details of the work of Austin, Hunt, Johnson and Parton are available; Oiwa claims a precision of a few tenths of a millivolt only; and the deviations from the preferred values are, with both sets of workers, in the sense to be expected if the hydrogen electrodes are not fully at equilibrium.

For the cell

$H_2|HBr|AgBr - Ag$, in water as solvent, the literature values are discrepant, though not seriously. Harned and Donelson[7] claimed that the difference between totally thermal electrodes, as used in all the investigations here quoted, and thermal-electrolytic electrodes as used in this investigation, was never greater than 0.04 mv. over a temperature range of 0°-50°.

It is quite impossible to prefer any one measurement to any other on a priori grounds, and accordingly the mean of four values is used:

0.07105 volts[8]
0.07133 volts[7]
0.07131 volts[9]
0.07106 volts[10]

Mean 0.0712 volts (± 0.13mv.) for E^o_m.

For the cell

$$H_2|\,HI\,|\,AgI-Ag$$

E^o_m (water)= -0.15225 volt[11]

Table 1

Wt % MeOH	Dielectric constant(ϵ)	Vapour pressure(π)	Density (ρ)	Mean mol. wt. M_{xy}
10	74.18	33.7	0.9799	18.84
43.12	59.40	66.0	0.9257	22.19

Table 2. Bromide systems

10% Systems.			43.12% systems.		
Molality of HBr,m	$E_{corrected}$ (volts)	$E^{o'}$ (volts)	Molality of HBr,m	$E_{corrected}$ (volts)	$E^{o'}$ (volts)
0.004683	0.34601	0.06640	0.004304	0.34104	0.05588
0.004760	0.34521	0.06639	0.005775	0.33026	0.05594
0.004842	0.34434	0.06638	0.006271	0.32264	0.05593
0.005184	0.34105	0.06644	0.008147	0.30976	0.05568
0.005695	0.33647	0.06650	0.008923	0.30569	0.05600
0.009409	0.31163	0.06634	0.009765	0.30132	0.05600
0.012020	0.29943	0.06617	0.016048	0.27716	0.05559
0.015050	0.28843	0.06608	0.031914	0.24477	0.05552
0.017071	0.28231	0.06605	0.035591	0.23937	0.05525
0.017953	0.27991	0.06615	0.051270	0.22223	0.05491
0.025590	0.26253	0.06580	0.075270	0.20444	0.05466
0.027500	0.25908	0.06578			
0.034649	0.24785	0.06558			
0.046190	0.23414	0.06550			
0.056871	0.22384	0.06502			
0.063706	0.21838	0.06485			
0.089708	0.20155	0.06405			

Table 3. Values of constants in Debye-Hückel expressions.

	10%	43.12%
A	0.5516	0.7698
B	0.3383	0.3780
B'	0.22_9	0.16_2
$\mathring{a}$	4.4	4.4

Table 4. Mean ion activity coefficients of HBr at rounded molalities.

m	10%	43.12%
0.002	0.950	0.932
0.005	0.925	0.899
0.01	0.901	0.866
0.02	0.872	0.827
0.05	0.830	0.767
0.10	0.801	0.722

Table 5 Iodide systems.

m	E_I	E_{Cl}	pK'	E°_m
10% MeOH				
0.002	0.55403	0.92314	9.265	-0.15376
0.003	0.54398	0.91332	9.277	-0.15399
0.004	0.53682	0.90620	9.280	-0.15403
0.005	0.53125	0.90052	9.282	-0.15392
0.007	0.52271	0.89216	9.286	-0.15410
0.010	0.51346	0.88304	9.287	-0.15423
43.12% MeOH				
0.002	0.56920	0.91384	9.438	-0.14884
0.003	0.55980	0.90427	9.455	-0.14867
0.0035	0.55555	0.90056	9.458	-0.14921
0.004	0.55241	0.89725	9.460	-0.14904
0.005	0.54670	0.89138	9.458	-0.14888
0.006	0.54210	0.88690	9.461	-0.14900
0.007	0.53810	0.88288	9.460	-0.14898
0.010	0.52910	0.87396	9.464	-0.14906

Table 6 **Summary of E_m^0 values.**

Solvent	HCl	HBr	HI
Water	0.22240	0.07120	-0.15225
10% MeOH	0.21535	0.06655	-0.15400
43.12% MeOH	0.19580	0.05600	-0.14985

Table 7 **Dissociation constants of boric acid.**

Solvent	pK
Water	9.234
10% MeOH	9.270
43.12% MeOH	9.449

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4. Discussion

The chemical potential, μ_i, of an ion i in solution, in the presence of other solute species j,k, ..., may be defined at a constant temperature T and pressure P, as :

$$\left(\frac{\partial G}{\partial n_i}\right)_{P,T,j,k...} = \mu_i = \mu_i^o + RT\ln a_i \qquad (1)$$

where μ_i^o is its chemical potential in the standard state, and a_i its activity with respect to that standard state.

Since it is, in general, possible only to measure the changes in free energy of processes which leave the solution electrically neutral, no experiment may be devised by which any of the quantities in equation (1) may be determined. This equation, while having mathematical meaning, has therefore no physical meaning. The change in free energy occurring when a pair of ions of opposite sign, e.g. H^+ and Cl^-, undergo a process, may be measured, as may that which happens when one ion is replaced by another of the same sign, as in the reaction which is the basis of the acidity function of Hammett:

$$B + H^+ \rightleftarrows BH^+ \qquad (2)$$

As all real processes involving ions in solution are subject to the restriction of electroneutrality, it is often sufficient to correlate experimental results by studying a suitable model process and comparing it with the system under investigation. Hence the application of acidity functions in studying the kinetics of acid-catalysed reactions, in which equilibria analogous to (2) may be involved.

It is mainly from the theoretical point of view that it is of interest to attempt the separation of thermodynamic quantities for pairs of ions into individual ionic values. This separation will be attempted here using the present experimental results.

Consider the information obtainable from the cells

$H_2|HCl|AgCl-Ag$ I

$H_2|HCl|Hg_2Cl_2-Hg$ II

Let ${}^{w}E^{o}$ and ${}^{s}E^{o}$ be the standard e.m.f.s. of either cell in water and in the mixed solvent respectively.

Put $\Delta G_t^o = F({}^{w}E^{o} - {}^{s}E^{o}) = F\Delta E^{o}$ (3)

ΔG_t^o, the free energy of transfer in the standard state (which remains to be chosen), is the difference between the combined solvation energies of 1 gm. ion of protons and 1 gm. ion of chloride ions in the two solvents. Put in another way, it is the total free energy change which occurs when these quantities of ions are transferred from one solvent to the other. Although it is necessary to specify a finite concentration in the standard state, the solution has otherwise the properties of a solution at infinite dilution, in that only ion-solvent and no ion-ion interactions are present.

In this account we concentrate largely on the changes in thermodynamic quantities occurring at 25° for 1 mole of various pairs of ions when they are transferred from aqueous solution to mixtures of water with 10% and 43.12% methanol by weight. Table I displays values of ΔE^{o} on the molal, molar and mole fractional scales (ΔE_m^o, ΔE_c^o and ΔE_N^o) obtained from cells I, II, III and IV :

$H_2|HBr|AgBr-Ag$ III

$H_2|HI|AgI-Ag$ IV.

and amalgam cells[1], for the halogen acids and alkali metal chlorides. ΔE^o_m is the primary experimental quantity, but ΔE^o_c has been selected for discussion for reasons which will be explained later, and ΔG^o_t (c) (= $F\Delta E^o_c$), the free energy of transfer on the molar scale, is also included.

Table I

Electrolyte	ΔE^o_m	ΔE^o_c	ΔE^o_N	$\Delta G^o_t(c)$
Water to 10% methanol transfer				
HCl	0.00705	0.00780	0.00475	180
HBr	0.00465	0.00540	0.00235	125
HI	0.00175	0.00250	-0.00055	58
LiCl	0.0140	0.0148	0.0125	341
NaCl	0.0189	0.0197	0.0174	454
KCl	0.0202	0.0210	0.0187	484
Water to 43.12% methanol transfer				
HCl	0.02660	0.0304	0.0159	701
HBr	0.01520	0.0190	0.0045	438
HI	-0.00330	0.0005	-0.0110	12
LiCl	0.0621	0.0659	0.0514	1520
NaCl	0.0858	0.0896	0.0751	2066
KCl	0.0940	0.0978	0.0833	2256

ΔE values in volts; ΔG values in calories.

For transfers from water to 10% methanol, the ΔE_t^o values for the hydrogen halides are accurate to about ± 0.2mv, and the ΔG values to ± 4k.cals. For the transfers from water to 43.12% methanol, the corresponding accuracies are ± 0.5mv. and ± 10k cals. The measurements on the alkali metal chlorides are subject to the uncertainties attendant on the use of amalgam electrodes, but are provisionally assumed to be of a similar order of accuracy.

A convention is required for the thermodynamic quantities. ΔG_t^o here has the meaning

$$\Delta G_t^o = {}^sG^o - {}^wG^o \qquad (4)$$

and a positive value signifies that a given pair of ions is in a lower free energy state in water than in aqueous methanol, which is what would be predicted from Born's equation.

Born's equation is derived on the assumption that the ions may be treated as charged spheres in a continuous dielectric, with radii equal to the crystallographic values. The free energy of transfer is then calculated from the difference in the work done in charging the ions in the two solvents. For easy comparison with the data above, we may consider the corresponding expression for the difference in standard e.m.f.s., which is

$$\Delta E^o = \frac{Ne^2}{2F}\left[\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w}\right]\left[\frac{1}{r_+} + \frac{1}{r_-}\right] \qquad (5)$$

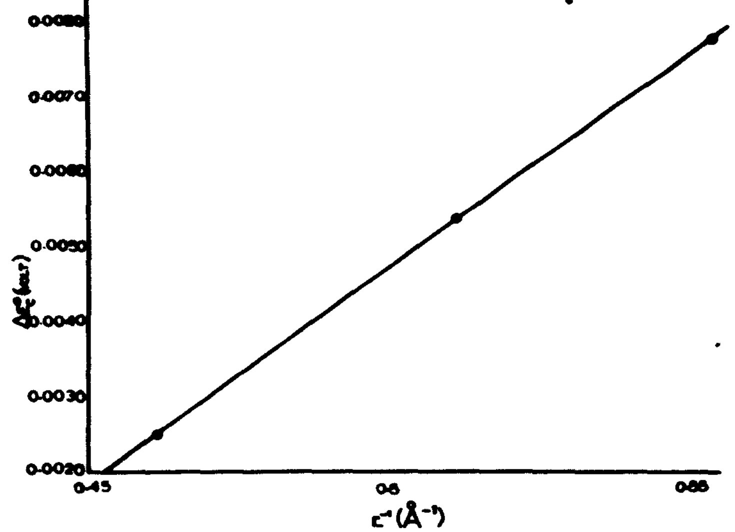
ϵ_s and ϵ_w are the dielectric constants of the mixed solvent and water respectively, r_+, r_-, the cationic and anionic radii. This equation may be tested in two ways.

Firstly, for a given electrolyte, i.e. for a given r_+ and r_-, ϵ_s may be varied. The plot of ΔE^o against ϵ_s^{-1} should then be linear. This point has been exhaustively examined for hydrochloric acid in a number of aqueous-organic solvent mixtures[2], and the test is hopelessly failed. The plots are rarely straight lines, and an individual one is usually required to describe the behaviour of the mixtures of each organic solvent with water. The paper of Feakins and French[2] may be consulted for a fuller discussion. In this it is also shown that a good correlation is achieved for a large number of different solvent systems of high water content between ΔE_c^0 and $\log \phi$ w, where ϕ is the volume fraction of water in the mixture. Methanol-water mixtures show this correlation particularly well, over a wide range of water concentrations. This behaviour was rationalised by assuming specific solvation of the ions by water molecules. The "solvation number" so obtained is suspiciously low (c.2) and while the reality of the stoicheiometric relationship cannot be denied, it is certain that the premises on which it is based are too naive. Bell and Robinson[3] find a similar relationship for pKs of weak acids in dioxan-water mixtures, and regard this as diagnostic of a mainly short-range ion-solvent interaction. This is also implicit in the treatment of Feakins and French.

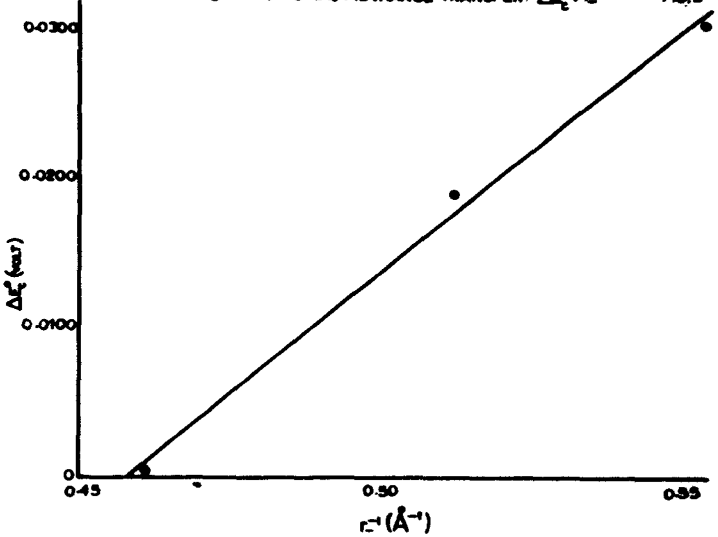
Secondly, for transfers from water to a given mixed solvent, e.g. the 10% or 43.12% mixture, the effect of variation of ionic radius may be studied. The ionic radii used, which are Pauling's, are in Table II.

Table II Ionic radii in Å.

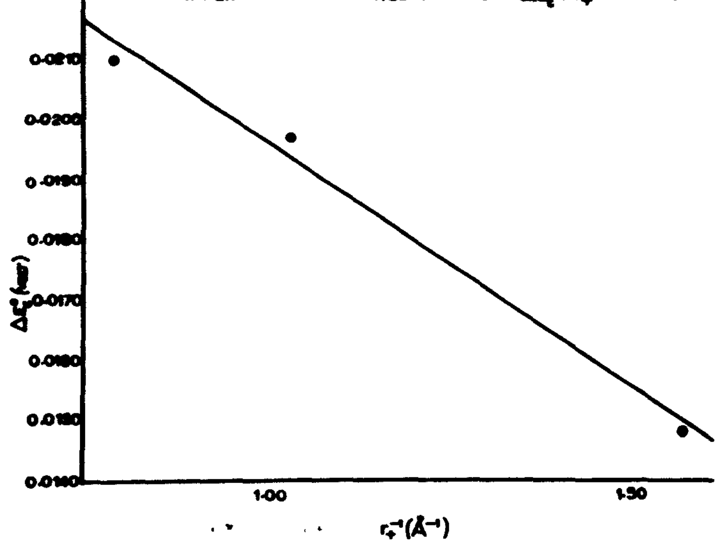
Ion	Li^+	Na^+	K^+	Cl^-	Br^-	I^-
r	0.607	0.958	1.331	1.806	1.951	2.168



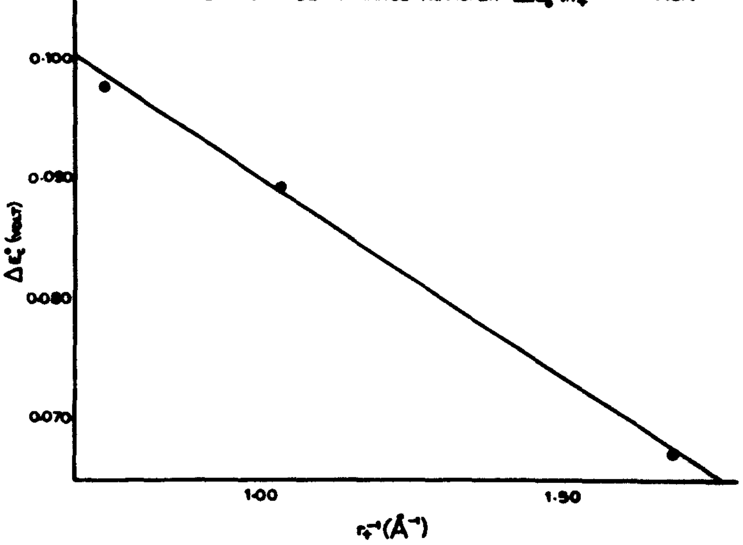
WATER ⟶ 10% METHANOL TRANSFER. ΔE_c° v. r_-^{-1} FIG.1



WATER ⟶ 43·12% METHANOL TRANSFER: ΔE_c° v r_-^{-1} FIG.2



WATER ⟶ 10% METHANOL TRANSFER: ΔE_c° v. r_+^{-1} FIG.3



WATER ⟶ 43·12% METHANOL TRANSFER. ΔE_c° v. r_+^{-1} FIG.4

Let us first examine the effect of plotting ΔE_c^o for the halogen acids against r_-^{-1}. It will be shown that for these transfers fairly good straight-line relationships hold, of the form :

$$\Delta E_c^o = b + \frac{a}{r_-} \qquad (6).$$

It is first required to justify the choice of ΔE_c^o for examination. If the quantity Fb does not contain any radius-independent contribution to the free energy of the anions, then it may be identified with the free energy of transfer of the proton. As r_- tends to large values, and ΔE_c^o tends to b, it is reasonable to suppose that the solutions are best described by volume fraction statistics. Under these circumstances, the free energy of transfer vanishes for $r_- = \infty$ if the transfer is made between the molar standard states.

Figures 1 and 2 show plots of ΔE_c^o against r^{-1} for the transfers of the hydrogen halides from water to 10% and 43.12% methanol respectively. In the case of the transfer to 10% methanol this is seen to be a good straight line from which the mean deviation of the points (± 0.02 mv.) is less than the experimental error. In the case of the transfer to 43.12% methanol the deviations from linearity (± 0.8 mv) are somewhat greater than the experimental error, and a curve through the three points is slightly concave towards the axis of r_-^{-1}. For the moment we shall ignore any deviation from linearity in figure 2.

The observed slopes are 5.72×10^{-2} volt Å and 3.25×10^{-1} volt Å respectively. The slopes predicted by equation (5) are 5.4×10^{-3} volt Å, and 2.9×10^{-2} volt Å, which in both cases are incorrect by a factor of about 10. Lest it should be thought that this is due to some peculiarity of the mixed solvent systems, it may be noted that a similar treatment of Mukherjee's[4] results for transfers from water to (nominally) pure ethanol at 35°, gives a line with a slope of about 4.3 times that predicted by the Born equation. We thus conclude, firstly, that the Born treatment may be incorrect by an order of magnitude.

Secondly, the values of b, which may now be regarded as the difference in standard potential of the proton in water and the mixed solvents, ΔE^{o}_{c} (H), obtained by extrapolation of these lines are -0.0239 (± 0.0002) volt, and -0.1487 (± 0.0050) volt respectively, in other words, both mixtures are more basic than is water itself. This result is the opposite of that predicted by equation (5).

Thirdly, the changes in standard potential for the chloride ion ΔE^{o}_{c} (Cl) which may be obtained by difference, are respectively + 0.0317 (± 0.0002) volt and + 0.1791(± 0.0050) volt. These, though in the sense predicted by (5), are about an order of magnitude greater. These values strikingly indicate the danger of ignoring the solvation of the negative ion.

If we plot ΔE^{o}_{c} for the alkali metal chlorides against r_{+}^{-1} (Figs. 3 and 4), we again find approximate straight line relationships, of the form

$$\Delta E^{o}_{c} = d + \frac{c}{r_{+}} \qquad (7)$$

This time, the slopes of the two lines are respectively -7.1×10^{-3} and -3.6×10^{-2} volt Å. These are incorrect in sign, an anomaly noted by Åkerlöf[1] and Gurney[5].

Suppose we form the concept that, for whatever reasons, the mixed solvents are more basic than water. We may expect that there will be a degree of analogy between the interaction of all positive ions with the solvents, and all will be more stable in the mixed solvents than in water itself to an extent, for a given charge, inversely proportional to their radii. This behaviour which is exactly the reverse of that predicted by equation (5), will lead to negative values of c.

The quantity d may now be identified with ΔE_c^o (Cl). The values obtained are, respectively, + 0.0267 (± 0.0009) volt and + 0.1261 (± 0.0025) volt. The values from the two sets of extrapolations are fairly close, and the agreement between them may be thought to confirm the validity of this approach.

Before proceeding, some comment on the reliability of these extrapolations is desirable. None of these graphs can be taken as proof that the correct dependence on crystallographic radius has been found. It is felt that the plots of ΔE_c^o against r^{-1} are acceptable since firstly, they give fairly concordant values of the single ion quantities, and secondly, they are physically reasonable. The mean values of ΔE_c^o (Cl) obtained from the r^{-1} plots are + 0.029 (± 0.0025) volt and +0.153 (± 0.026) volt respectively,and these are used as bases for the separation of ΔE_c^o values for pairs of ions into the individual ionic values displayed in Table III. The ionic free energies of transfer are in Table IV.

Table III Individual ionic values of ΔE_c^o

Ion	Water → 10% methanol ΔE_c^o (volts)	Water → 43.12% methanol ΔE_c^o (volts)
H^+	-0.021	-0.123
Li^+	-0.014	-0.087
Na^+	-0.009	-0.063
K^+	-0.008	-0.055
Cl^-	+0.029	+0.153
Br^-	+0.027	+0.142
I^-	+0.024	+0.123

Table IV Ionic free energies of transfer, ΔG_c^o

Ion	Water → 10% methanol ΔG_c^o (cals)	Water → 43.12% methanol ΔG_c^o (cals).
H^+	-490	-2800
Li^+	-330	-2000
Na^+	-220	-1400
K^+	-190	-1200
Cl^-	+670	+3500
Br^-	+620	+3200
I^-	+550	+2800

We shall discuss transfers from water to other solvents only briefly. Åkerlöf's measurements on the alkali metal chlorides cover a range of aqueous mixtures containing from 0-90% methanol by weight. These may be treated in the above fashion to give ΔE_c^o (Cl) and then combined with results from cell I to give values of ΔE_c^o(H). These show that in higher concentrations of methanol, as well as in those already studied, there is a steady increase in basicity of the solvent as the proportion of methanol is increased. It is hoped, in subsequent work, to confirm this by studies of cells III and IV, so that figures will not be quoted at this stage.

The situation in pure methanol is difficult to assess. Reliable values of ΔE_c^o for the water to methanol transfer are available only for hydrochloric and hydrobromic acids. Extrapolation of these yields $\Delta E_c^o(H) = -0.14$ volt. Solubility measurements on sodium and potassium chlorides give the poorly concordant $\Delta E_c^o(H) = -0.27$ volt. Thus methanol seems to be a stronger base than water, but the transfer of the chloride ion from water to methanol is strongly disfavoured ($\Delta E_c^o(Cl) \simeq 0.4$ volt). Similarly, Mukherjee's results give ΔE_c^o (H) $= -0.44$ volt and $\Delta E_c^o(Cl) = +0.63$ volt for ethanol at 35°, and though it is doubtful whether his solvent was really dry, ethanol appears also to be a stronger base than water.

We shall now consider the enthalpies and entropies of transfer between water and the mixed solvents. Slansky[6] has determined heats of solvation of a number of alkali halides together with hydrogen chloride, in water, methanol and their mixtures.

All the enthalpies of transfer vary in much the same way with change in solvent composition. Unlike the free energies of transfer which vary monotonically with solvent composition[1],[2] the enthalpies are such as to disfavour the transfer from water to solvents of low methanol concentration, but to favour that to solvents of high methanol concentration. The most disfavoured transfers are those to solvents containing between 20% and 30% methanol.

In table V are collected the ΔG, ΔH and $-T\Delta S$ values for transfers from water to the two mixtures, using the same sign convention as before.

Table V

Electrolyte	ΔG_t^o (cals)	ΔH_t^o (cals)	$-T\Delta S_t^o$ (cals)
Water to 10% methanol transfer.			
HCl	180	330	-170
HBr	125	320	-200
HI	58	260	-200
LiCl	341	900	-560
NaCl	454	480	-25
KCl	484	290	+195
Water to 43.12% methanol transfer.			
HCl	701	880	-180
HBr	438	570	-130
HI	12	190	-180
LiCl	1520	650	870
NaCl	2066	680	1390
KCl	2256	375	1880

Some of the ΔH values must be regarded with reserve. There are several instances of non-additivity of individual ionic values in Slansky's figures and the values of ΔH quoted for the halogen acids are obtained from those for hydrochloric acid, and means of the values for the sodium and potassium halides. These observations are not intended to detract from the value of Slansky's work.

If any further proof of the inapplicability of Born's approach were required, these figures supply it. For example, for the transfer from water to 10% methanol-water, the predictions of equations (5) and (8)

$$\Delta S = \frac{Ne^2}{2}\left[\frac{1}{\epsilon_s^2}\left(\frac{\partial \epsilon_s}{\partial T}\right) - \frac{1}{\epsilon_w^2}\left(\frac{\partial \epsilon_w}{\partial T}\right)\right]\left[\frac{1}{r_+} + \frac{1}{r_-}\right] \qquad (8)$$

are ΔG = 276 cals., ΔH = -449 cals., and $-T\Delta S$ = 725 cals. for lithium chloride.

No obvious basis exists for the separation of heat and entropy data into individual ionic values. Although the enthalpy values vary monotonically with r^{-1} within the alkali metal chloride or halogen acid series, extrapolations similar to those used above give completely different single ion values in the two cases. Though it is possible that this behaviour is due to inaccuracies in the primary enthalpy data, arguments developed later give possible reasons for it.

Let us now summarise the main conclusions so far :

(1) 10% and 43.12% mixtures of methanol with water are stronger bases than water, and so are probably all methanol-water mixtures and pure methanol and ethanol.

(2) Transfers of the halide ions from water to these solvents are disfavoured, and the free energies of transfer are an order of magnitude greater than those predicted by equation (5).

(3) In contrast, the alkali metal ions, and the proton, are more stable in these solvents than in water.

(4) The free energy of transfer of all the anions studied is greater numerically than for any of the cations, despite the lower radii of the latter. For the water to 10% methanol transfer, $\Delta G = +670$ cal. for the chloride ion, and $\Delta G = -90$ cal. for a hypothetical cation of the same radius.

(5) In contrast to the free energies of transfer, which vary smoothly and monotonically with ionic radius and solvent composition, the enthalpies and entropies do not.

Certain drastic assumptions are required to rationalise these observations. Let us assume that two types of interaction of an ion with a solvent are of dominant importance in the present case. Firstly, the ion affects the structure of the solvent in some way: in particular hydrogen bonds are made or broken, strengthened or weakened. Thus the ion affects the solvent-solvent interactions. Secondly, the ion has an electrostatic potential energy due to the interaction of its own charge with the charges on the solvent molecules. We include in this any attractive covalent interaction which could not, of course, be evaluated by Coulomb's law.

Insofar as the first effect is analogous to a freezing or melting process, for which $\Delta G = 0$, its contribution to the free energy of solvation of the ion may be taken as small, and will be neglected in the present treatment. This does not preclude large contributions to the free energy and enthalpy of solvation. This striking suggestion is due to Ives[7]. Its consequences may be briefly examined.

It is assumed that while the contribution of the first interaction to the free energy of transfer is negligible, the entropy and enthalpy of transfer will contain structural contributions which may be large. No analysis of these quantities will be attempted, but two points may be noted which support these contentions. Firstly, the enthalpies of transfer for pairs of ions show maxima at around 20-30% of methanol. This is a region in which the heats and excess entropies of mixing of methanol and water and the partial molar volume show minima, and the viscosity of the mixtures and the Walden product for the proton show maxima. Insofar as all these properties may be regarded as structural properties of the solvent mixtures, the enthalpy of transfer of ions appears to be related to them, while free energies of transfer, varying monotonically with solvent composition, do not.

Secondly, we consider the enthalpies of transfer for the alkali chlorides from water to 20%, 40%, 60%, 80% and 100% methanol (Table VI), The lack of any simple dependence on the cation radius will be noted, and in particular, the way in which even the numerical order of the enthalpies of transfer changes between different transfers. In this apparently haphazard

Table VI - Enthalpies of transfer, water to X% methanol in cals.

Electrolyte	20%	40%	60%	80%	100%
LiCl	1400	850	-100	-1050	-2400
NaCl	760	800	455	-420	-2920
KCl	490	420	-250	-1330	-3040
RbCl	290	350	150	-550	-2720
CsCl	210	100	-240	-1090	-2390

situation there is nonetheless a degree of analogy to certain properties of the alkali metal halide crystals.[8] If a particular property of these crystals is tabulated in numerical order for all the fluorides, this will place the alkali metal ions in a certain order, which, however, changes if the counter-ion is changed to chloride, bromide or iodide. This behaviour has been discussed by Pauling[8] in some detail, and can be rationalised by taking the repulsive forces in the crystal into account. While in a crystal, the observed behaviour is in part a function of changing the nearest neighbours of a cation from the fluoride ions to the larger iodide ions, that in the solutions may be due to a change in the nearest neighbours of the ions from water molecules to methanol molecules, or a mixture of the two, with corresponding changes in the repulsive forces between them.

We pass to the interaction of the charge on the ion with the charges on the solvent molecules. It is now assumed that the potential energy arising therefrom may be equated with the free energy of the ion in solution.

There are three properties of the water and methanol molecules which are relevant to the present discussion.

(1) The detailed charge distribution in the molecule. This is not known, but the inductive effect of the methyl group in the methanol molecule should increase the electron density on the oxygen atom and leave the hydroxyl hydrogen less positively charged in each case relative to the corresponding atoms in the water molecule.

(2) The dipole moment of the methanol molecule (1.69 D) is lower than that of the water molecule (1.87 D).

(3) The dielectric constants of methanol and of its mixtures with water are lower than that of water.

Consider the solvation of the proton. It will form a strong bond with one molecule of water in pure water, and one molecule of methanol in pure methanol to give the species H_3O^+ and $CH_3.OH_2^+$. Without speculating on how far the new bond is "ionic" and how far it is "covalent", it is reasonable to suppose that its strength is determined largely by the charge density on the original unprotonated molecule, and therefore that it is stronger in $CH_3.OH_2^+$ than in H_3O^+. This primary solvation of the proton will stabilise it in methanol with respect to water, and presumably this stabilisation extends also to methanol-water mixtures, wherein the protons are presumably distributed among both sorts of molecules. Specific primary solvation of the proton by water molecules in methanol-water mixtures must be abandoned.

Two points may be noted. Firstly, the fact that the H_3O^+ ion can form four hydrogen bonds while the $CH_3OH_2^+$ ion can only form two is not a factor that will stabilise the former with respect to the latter, because these are precisely the numbers of bonds that were being formed by the original solvent molecules before protonation. The only change is that in both cases the ionic species can form one more bond as an electron acceptor, and one bond fewer as an electron donor than the original molecule. Secondly, we suggest that a proton bonded to a water molecule could be indirectly stabilised by a methanol molecule bonded to the water molecule, since the methanol molecule may induce a negative charge on the oxygen atom of the water molecule. Indeed, such stabilisation might well extend over hydrogen-bonded chains of some length[9].

In exactly the same way, we may examine the primary solvation of a typical alkali metal ion. Here, the solvent molecules are no doubt oriented with their oxygen lone pair orbitals overlapping the acceptor orbitals (sp^3 or sp^3d^2) of the ions. Again, making no distinction between ionic and covalent bonding, the strength of the bond between the ion and the solvent molecules will depend on the electron density on the oxygen atom. Thus the primary solvation will also stabilise these ions in methanol with respect to water. In methanol-water mixtures, methanol no doubt enters the first solvation sheath of a proportion of the ions according to equilibria of the sort :

$$K(H_2O)_6^+ + MeOH \rightleftharpoons K(H_2O)_5\,MeOH^+ + H_2O$$

$$K(H_2O)_5\,MeOH^+ + MeOH \rightleftharpoons K(H_2O)_4(MeOH)_2^+ + H_2O$$

etc.

When the mole fraction of methanol is low, the probability of more than one methanol molecule entering a first solvation sheath, being proportional to the nth power of the mole fraction of methanol for the entry of n molecules, is extremely small. There will however be a net stabilisation of the ion in the methanol-water mixtures due to the primary solvation.

Much smaller free energy changes are likely to occur with any of these ions than with the proton, the centre of which can approach the negative centre of the solvating molecules more closely.

Considering both the proton and the other cations it may be supposed that in the region of secondary solvation immediately outside the first, the dielectric is saturated. This is partly because of the high field of the ion and partly because oriented solvent molecules in the first sheath will tend to orient those in the second through hydrogen bonding. In contrast to the situation in the first sheath, the detailed charge distribution of the molecule is less relevant and the interaction of the molecule and the ion is now well approximated by the formula :

$$V = \frac{-e\mu}{r^2}$$

where e is the charge on the ion, μ the dipole moment, and r the distance of the centre of the ion from the centre of the dipole. Secondary solvation of this type will stabilise the ion in water of higher dipole moment with respect to methanol (of lower dipole moment) or its mixtures with water, and oppose the effect of the primary solvation.

It is commonly supposed that somewhere in successive layers of solvent round the ion there exists a region where the solvent structure has been broken down, at least in water. Gurney[5] thought that all ions became net structure-makers as they passed from pure water to pure methanol, and indeed rationalised the apparently anomalous behaviour of the alkali chlorides solely in terms of the entropy changes arising from structural circumstances. It is precisely this explanation which is being rejected here: the suggestion is that the structural changes in the solvent make only a very small contribution to the free energy of transfer, although their contribution to the heats and entropies of transfer may be large.

We shall assume that this region comes outside the region of secondary solvation. It will be classed with the rest of the solvent as a region where the free energy of solvation could be computed by Born charging. It is unlikely that there is a substantial contribution from this region, since the effective sphere being charged is so large. Such long-range solvation would stabilise the ion in water relative to methanol or its aqueous mixtures.

The results show that the effect of the primary solvation outweighs that of the secondary and long range solvations for all the cations considered.

Consider the solvation of the halide ions. These will be surrounded by solvent molecules oriented in such a way that a hydrogen atom is immediately adjacent to the ion. The strength of the attraction between the ion and the solvent molecules will be dominated by the coulombic force between the charge on the ion and the charges on these hydrogen atoms, and accordingly the ion will be stabilised in water rather than methanol or its mixtures with water.

In the case of halide ions, the secondary and long-range solvations will have the same energetic consequences as the primary solvation. This will undoubtedly be one reason why the total free energy changes occurring on transfer of the halide ions, the sums of contributions from all regions, are much greater than the free energies of transfer for positive ions, which are differences between contributions from the various regions.

It is also possible, however, that the interaction between a halide ion and the solvent molecules in the first solvation sheath is actually stronger than would be found in the first solvation sheath of a cation of the same size. This is a view taken by Verwey[10], Latimer[11] and Buckingham[12], Verwey finding a difference of 47 k.cals/gm.ion. between the solvation energy of the potassium and fluoride ions in water, in favour of the fluoride ion. As this point of view depends again on the separation of solvation energies into individual ionic values, it has been challenged, but the present results are consistent with it. It is possible that the charge distribution in the molecules concerned is such that the charge is greater on a positive centre adjacent to an anion, or is nearer the centre of the ion, than is the case for the negative centre.

A much more detailed treatment would be needed to substantiate this analysis. When accurate quadrupole moments of molecules are available then it will be possible to apply the more formal approach of Buckingham to the problem. The physical basis of the present approach is very similar to that of Buckingham, Verwey and in particular Hudson and Saville[13]. The rather large order of the free energies of transfer in some cases remains to be explained, but it may be noted that two point electronic charges at a distance of 3Å apart have a mutual electrostatic energy of about 100 k.cals, and a variation of 1% in either charge changes this energy by 1 k.cal., a comparatively large amount in the present work.

Some doubt must remain about the validity of the extrapolations. In a realistic model, such as Buckingham's, the ionic free energies are complicated functions of the ionic radius, and it may seem that plots of free energy against the reciprocal of ionic radius are a gross oversimplification which may produce misleading results. At the same time, some experimental justification has already been given for this course. If the dominant term in the free energy is the attractive force between the charge on the ion and that on a charged centre (in a lone pair orbital or on a hydrogen atom) in an adjacent molecule, then there is also some theoretical justification for it. Such centres should be able to approach the surface of the ion quite closely, and thus the electrostatic interaction energy V, will be of the form

$$V = - \frac{|\delta e|\,|e|}{(r_i + \Delta r)}$$

where $|\delta e|$ is the charge on the relevant part of the molecule, and $|e|$ that on the ion, r_i is the ionic radius, and Δr is the distance of the charged centre of the molecule from the surface of the ion. Δr is impossible to estimate for the cations, but for the hydrogen atom is likely to be of the order of its covalent radius in water (0.3 Å). It makes very little difference to the results tabulated above if this quantity is added to the anion radii.

Priority for the discovery of the startling differences in behaviour between positive and negative ions in mixed solvent systems must go to Grunwald, Baughman and Kohnstam[14], whose important and elegant work must be briefly described to conclude this discussion.

Using a vapour pressure method they were able to measure a quantity

$$\left(\frac{dF_1}{dZ_1}\right)$$

which in our terminology would be $\left(\frac{dG_N^o}{dZ_1}\right)$ where Z_1 is the mole fraction of water in the dioxan-water mixtures. This quantity was measured for a number of electrolytes in a single mixture containing 50% by weight of dioxan. $\left(\frac{dG_N^o}{dZ_1}\right)$ should vary from ion to ion in much the same way as ΔG_t^o.

While for the alkali halides, hydrochloric acid and sodium hydroxide these measurements indicate that they are less stable in dioxan-water mixtures than in pure water as would be predicted from equation (5), this is not so for some other electrolytes, such as $(C_6H_5)_4PCl$, $NaB(C_6H_5)_4$ and perchloric acid. To the extent that the tetraphenylphosphonium and tetraphenylboride ions are analogous to tetraphenyl methane $C(C_6H_5)_4$ this behaviour is to be expected: their non-electrolyte characteristics outweigh their ionic characteristics.

It was possible to compute the quantity $\left(\frac{dG_N^o}{dZ_1}\right)$ for 1 mole of tetraphenyl-phosphonium tetraphenylboride, and after allowing for a small electrostatic effect, this was found to be not very different from the value for two moles of tetraphenyl methane. It seemed reasonable then, to equate $\left(\frac{dG_N^o}{dZ_1}\right)$ for these two ions and so obtain individual ionic values.

The conclusion drawn is that the proton and all the alkali metal cations are more stable in dioxan-water mixtures than in water itself, but that the reverse is true for the halide and hydroxide ions. The present work, in which the individual ionic values are obtained in a completely different way, shows that this pattern also holds for transfers from water to water-methanol mixtures.

To explain their results the authors use a "chemical" theory of solvation. The greater part of the free energy of transfer is attributed to the binding of solvent molecules to the ions with a consequent disappearance of their own free energy. Insofar as the chemical potentials of the components change with solvent composition, the free energy of solvation will also change. The authors reject specific solvation by water for cations (a view also adopted in the present work) and take the view that at least partial dioxanation must occur.

It will be apparent that our own interpretation is very different from this, but we do not wish as yet to compare the two interpretations, especially as the experimental conclusions are so strikingly similar..

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5. Dioxan-water mixtures.

So far only the cell

$$H_2|HBr|AgBr-Ag$$

has been studied in 20% dioxan-water mixtures.

Preliminary work took the form of developing a cell suitable for the measurement of e.m.f. over a temperature range and therefore over a long period of time. The results of this work are described in section 2.2. Provided that the samples of dioxan used to prepare the solutions are free from peroxide, as indicated by the potassium iodide test, good cell behaviour is found. Thus electrodes come to equilibrium quickly and the e.m.f. readings are steady in time. The measurements are normally begun at 25°, proceed by 5° intervals to 45°, then by 5° intervals to 5°, then by 5° intervals to 25°. At every temperature then, the cell equilibrates at least twice, and the difference in the values of the e.m.f. is normally less than 0.05 mv. The hydrogen electrode potentials are independent of the rate of bubbling of hydrogen.

All this would be very satisfactory were it not that, at the time of writing, the e.m.f. values appear to be markedly dependent on the preparation of the dioxan used in making the solution.

The preparation of the dioxan always begins with the same purification procedure.

2 litres of dioxan ("AnalaR") are refluxed with 25 ml. of concentrated hydrochloric acid and 200 ml. of distilled water for 12 hours while passing a slow stream of nitrogen gas through the mixture. The glycolacetal present as the chief impurity is

hydrolysed to acetaldehyde and this is swept out by the nitrogen stream.

When the acidified mixture is cool, an excess of potassium hydroxide is added with constant agitation, and causes separation into aqueous and dioxan layers. The dioxan is separated and allowed to stand over fresh potassium hydroxide for 24 hours.

Last traces of water and aldehyde are removed by refluxing the dioxan over freshly cut sodium for 12 hours, the aldehyde being resinified at this stage. The dioxane is then fractionally distilled from this sodium, the fraction boiling in the range 101.2 - 101.4° being collected, about 35 - 40% of the charge.

This material is stored over sodium in a nitrogen atmosphere and redistilled as required.

Cell solutions have been prepared from the following samples:

(1) Dioxan distilled directly from the column into the solution flask.

(2) Dioxan which has been kept for a few hours under nitrogen but is free from peroxides.

(3) Dioxan which has been kept for longer periods and contains varying amounts of peroxides. This is now known to be quite unsuitable for measurements.

(4) Dioxan which has been purified as above and then passed through a column of carefully purified activated alumina. According to Dasler and Bauer[2], this treatment removes all peroxidic materials.

It is not yet clear whether samples (1) and (2) give different results, but solutions prepared from dioxan of type (4) give very different results from those prepared from type (2). The solutions are made up to have molalities of HBr fairly close to each other and the function $E^{0'}$ (section 3.12) is then computed from the observed e.m.f. values at the various temperatures. If the dioxan used is of type (4) then the $E^{0'}$ values are some 5 mv. lower than is the case when dioxan of type (2) is used. The freezing-points of the two samples are used as criteria of purity, and are identical to within 0.03°.

If the two samples are used to prepare cell solutions containing 20% dioxan and hydrochloric acid and the corresponding cell with silver-silverchloride electrodes is used, then solutions prepared from type (2) give very good agreement with the values given by Harned and co-workers, but solutions prepared from type(4) give e.m.f. values which are 15 mv. lower.

The reason for this must lie in the solution of some impurities, probably ionic, by the dioxan as it passes through the column of alumina. Although the conductance of samples diluted with conductance water has been checked, this would only reveal a gross contamination unless done under very carefully controlled conditions. The determination of the freezing-point, similarly, is not sufficiently sensitive to reveal contamination in amounts enough to upset the e.m.f. measurements.

It has therefore been decided to examine the reproducibility of a series of measurements made with freshly distilled dioxan, and these are now under way.

References

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6. Future research plans.

This report reveals the extent of the experimental difficulties which must be overcome before the systems of interest can be studied, and clearly an effort extending over many years is required before deep inroads into a subject which has hitherto been neglected can be made. It is felt that this is a topic which is best pursued by a small group over a long period of time rather than by a large group over a short period of time.

The immediate objectives are quite clear. The thermodynamic work in methanol-water mixtures must be extended to cover the whole range of solvent compositions, because these are the systems for which complementary data is available in the literature.

In the dioxan-water mixtures it is hoped at the moment to concentrate on thermodynamic work in a particular solvent system, the mixture of 20% dioxan with water, and study the pairs of ions: $H^+ Br^-$, $H^+ I^-$, possibly H^+F^-, and Li^+Cl^-, Na^+Cl^- and K^+Cl^- by the amalgam cells.

It would then be highly desirable to have Washburn number data for the methanol-water systems. At the moment, Washburn number data are only available for solutions in which the water content is high, and in these solutions, the net transport of water would be towards the negative electrode in an electrolysis. This is not unexpected : because of their generally smaller radii cations will move more solvent than anions, and on statistical grounds (see Discussion section) there will be a net preferential solvation of the ions by water molecules. As the proportion of methanol in the mixture increases, however, the balance should swing in favour of preferential solvation of cations by methanol molecules and of anions by water molecules, and the net transport of water should be towards the positive electrode in an electrolysis, if the assumptions made to explain the thermodynamic properties are correct.

Looking further ahead, it should be profitable to study the thermodynamic properties of electrolytes in a range of pure non-aqueous solvents, about which there is at the moment a paucity of data.

7. Annex

1) Personnel utilised during the reporting period.

Paul Watson, B.Sc. (Whole period)
David J. Turner, B.Sc.(Whole period)
Nicholas J.Dennis,B.Sc.(23rd July - 30th September)

2) (a) Manhours expended

By the personnel mentioned above a total of some 5,200 manhours. In addition the principal investigator has devoted considerable time to theoretical and practical aspects of the work.

(b) Expenses for materials used

£322 ($902) has been expended.

(c) Important apparatus acquired at direct contract expense

None.